Molecular Electronics Devices Using Vapor Phase Assembly

Lloyd R. Harriott
Professor and Chair
lrharriott@virginia.edu

www.ece.virginia.edu

ITRS 2005 – Emerging Research Devices

http://public.itrs.net

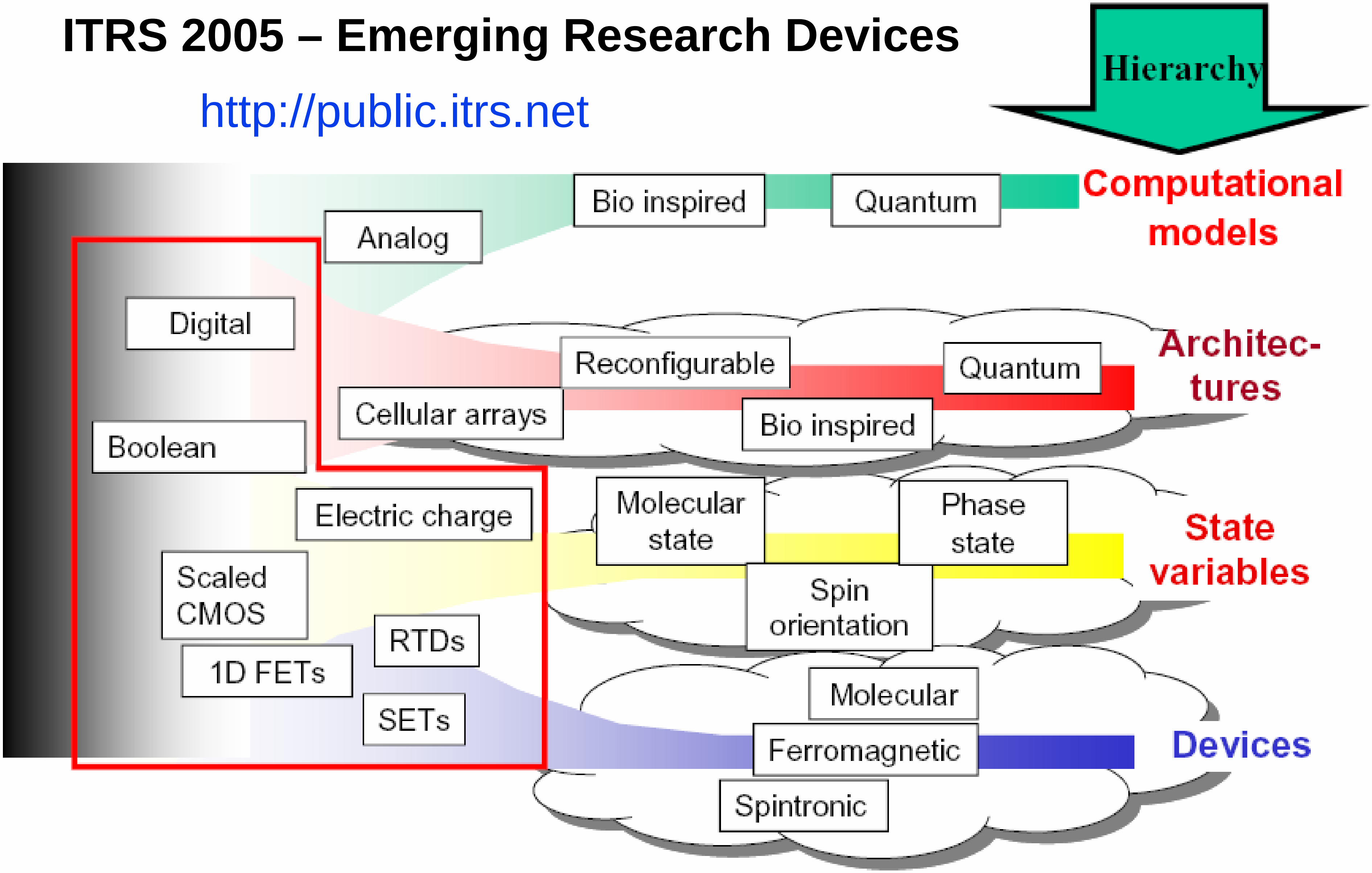
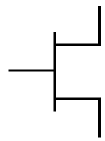
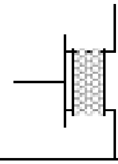
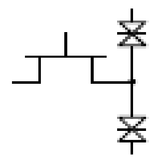
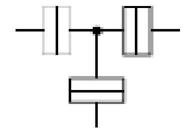
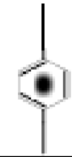
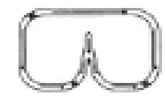
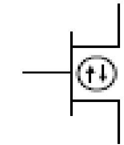


Figure 51 A Taxonomy for Nano Information Processing

Table 59 Emerging Research Logic Devices—Demonstrated Projected Parameters

Device								
		FET [B]	*1D structures*	*Resonant Tunneling Devices*	*SET*	*Molecular*	*Ferromagnetic logic*	*Spin transistor*
Types		*Si CMOS*	*CNT FET* *NW FET* *NW hetero-structures* *Crossbar nanostructure*	*RTD-FET* *RTT*	*SET*	*Crossbar latch* *Molecular transistor* *Molecular QCA*	*Moving domain wall* *M: QCA*	*Spin transistor*
Supported Architectures		*Conventional*	*Conventional and Cross-bar*	*Conventional and CNN*	*CNN*	*Cross-bar and QCA*	*CNN Reconfigure logic and QCA*	*Conventional*
Cell Size (spatial pitch)	*Projected*	**100 nm**	**100 nm [C]**	**100 nm [C]**	**40 nm [L]**	**10 nm [Q]**	**140 nm [U]**	**100 nm [C]**
	Demonstrated	**590 nm**	**~1.5 μm [D]**	**3μm [H]**	**~700 nm [M]**	**~2μm [R]**	**250 nm [V, W]**	**100 μm [X]**
Density (device/cm^2)	*Projected*	**1E10**	**4.5E9**	**4.5E9**	**6E10**	**1E12**	**5E9**	**4.5E9**
	Demonstrated	**2.8E8**	**4E7**	**1E7**	**2E8**	**2E7**	**1.6E9**	**1E4**
Switch Speed	*Projected*	**12 THz**	**6.3 THz [E]**	**16 THz [I]**	**10 THz [M]**	**1 THz [S]**	**1 GHz [U]**	**40 GHz [Y]**
	Demonstrated	**1 THz**	**200 MHz [F]**	**700 GHz [J]**	**2 THz [N]**	**100 Hz [R]**	**30 Hz [V, W]**	**Not known**
Circuit Speed	*Projected*	**61 GHz**	**61 GHz [C]**	**61 GHz [C]**	**1 GHz [L]**	**1 GHz [Q]**	**10 MHz [U]**	**Not known**
	Demonstrated	**5.6 GHz**	**220 Hz [G]**	**10 GHz [Z]**	**1 MHz [F]**	**100 Hz [R]**	**30 Hz [V]**	**Not known**
Switching Energy, J	*Projected*	**3E-18**	**3E-18**	**>3E-18**	1×10^{-18} **[L]** [$>1.5\times10^{-17}$] **[O]**	**5E-17 [T]**	**~1E-17 [V]**	**3E-18**
	Demonstrated	**1E-16**	**1E-11 [G]**	**1E-13 [K]**	8×10^{-17} **[P]** [$>1.3\times10^{-14}$] **[O]**	**3E-7 [R]**	**6E-18 [W]**	**Not known**
Binary Throughput, GBit/ns/cm^2	*Projected*	**238**	**238 [C]**	**238 [C]**	**10**	**1000**	**5E-2**	**Not known**
	Demonstrated	**1.6**	**1E-8**	**0.1**	**2E-4**	**2E-9**	**5E-8**	**Not known**
Operational Temperature		**RT**	**RT**	**4.2 – 300 K**	**20 K [L]**	**RT**	**RT**	**RT**
Materials System		**Si**	**CNT,** **Si, Ge, III-V,** In_2O_3**, ZnO,** TiO_2**, SiC,**	**III-V** **Si-Ge**	**III-V** **Si**	**Organic molecules**	**Ferromagnetic alloys**	**Si, III-V, complex metals oxides**
Research activity [A]			**171**	**88**	**65**	**204**	**25**	**102**

UVA Team

• Lloyd Harriott	ECE	Nanofabrication
• John Bean	ECE	Processing
• Lin Pu	Chem	Synthesis
• Matt Neurock	ChE	Modeling
• Nathan Swami	ECE	Electrochemistry
• Avik Ghosh	ECE	Theory
• Keith Williams	Physics	Spectrscopy

External Collaborators

• Mark Reed	Yale ECE	Devices
• James Tour	Rice Chem	Molecules
• Curt Richter	NIST	Testing

Funding Support

National Science Foundation NIRT Program
DARPA – MoleApps Program

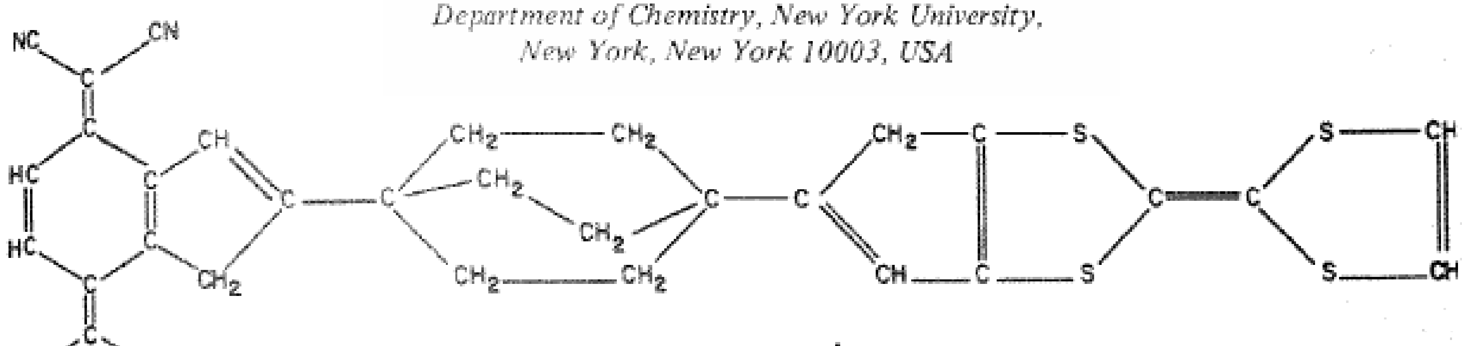
Volume 29, number 2 CHEMICAL PHYSICS LETTERS 15 November 1974

MOLECULAR RECTIFIERS

Arieh AVIRAM
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, USA

and

Mark A. RATNER*
Department of Chemistry, New York University, New York, New York 10003, USA



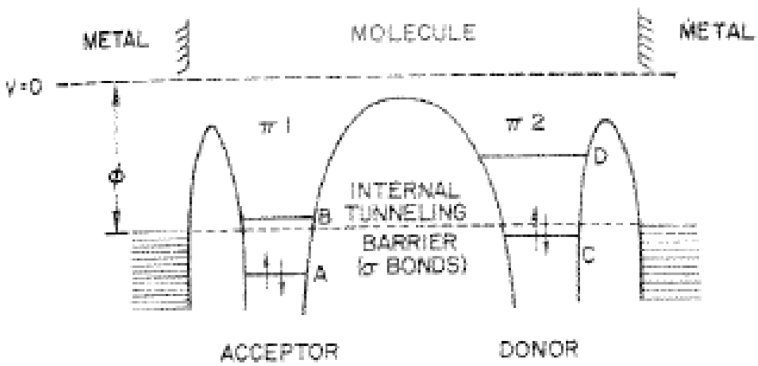


Fig. 3. Energy versus distance of the device (schematic). B and D are the affinity levels and A and C the highest occupied levels, of acceptor and donor, respectively.

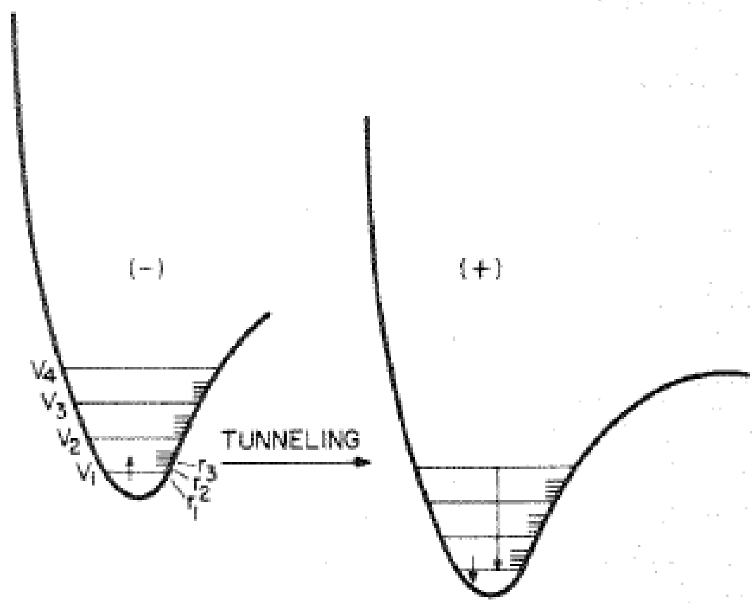
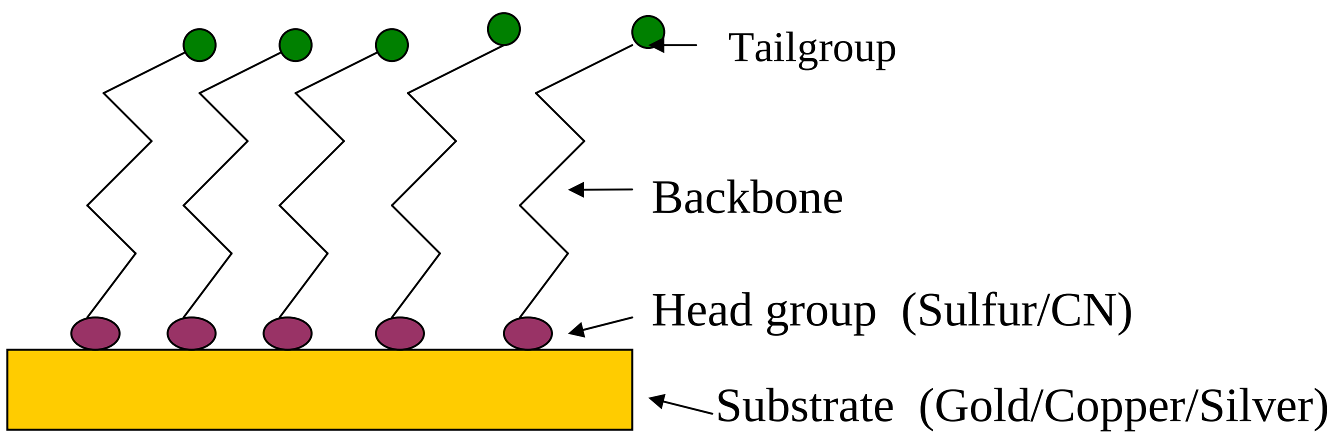


Fig. 5. Internal tunneling.

Why has it taken so long?

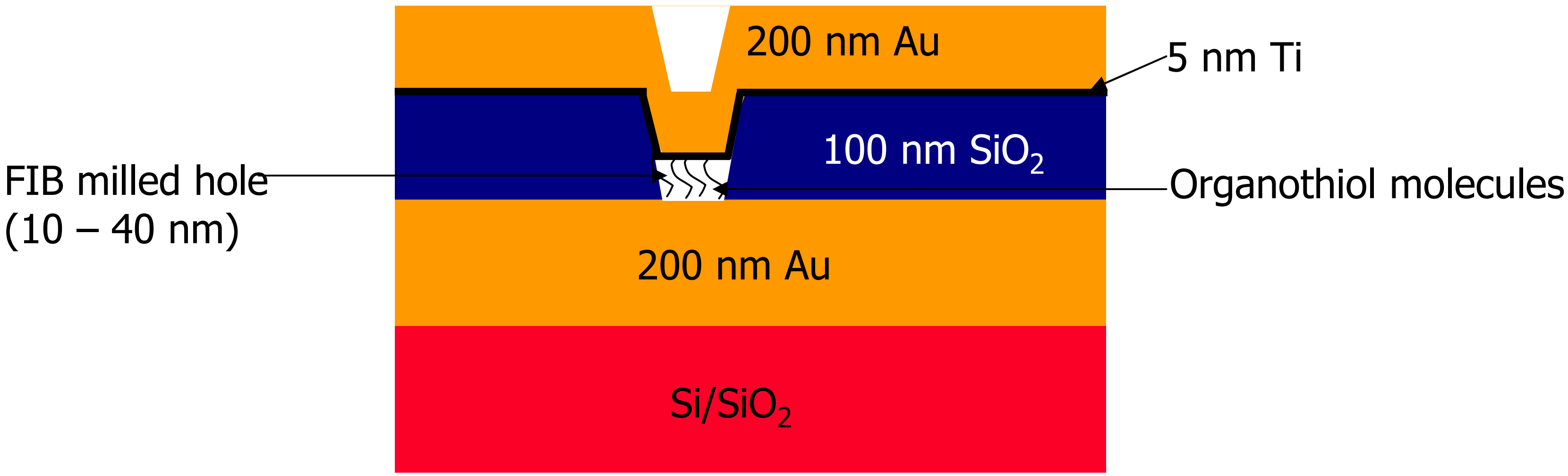
- **Difficult to attach "wires" to a single or small number of molecules:**
  - **Self-Assembled Monolayers – Solution and Vapor Phase**
  - **"Top" contact by: SPM, Break Junction, Nanopore**
  - **Not Integrable to circuit**
  - **Tunneling, rectification, NDR, switching, etc. shown**



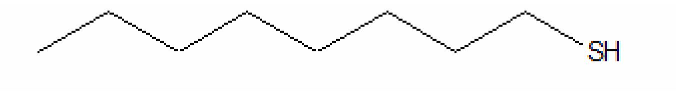
Molecular Electronics at UVA

- Develop Planar Device Structure and Processes
- Evaluate candidate molecules
- Study transport and switching mechanisms
- Develop Circuit models and fabrication schemes
- Develop new fabrication methods – Vapor Phase
- Simulate Circuit Performance based on device data
- Feedback to synthesis and fabrication for improved circuit yield and performance

Nanowell Device

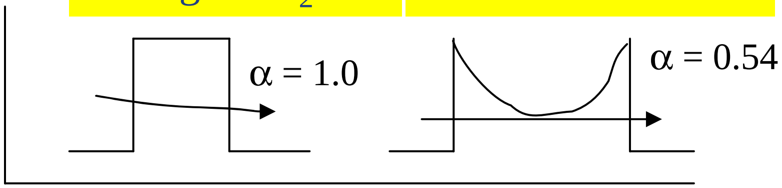


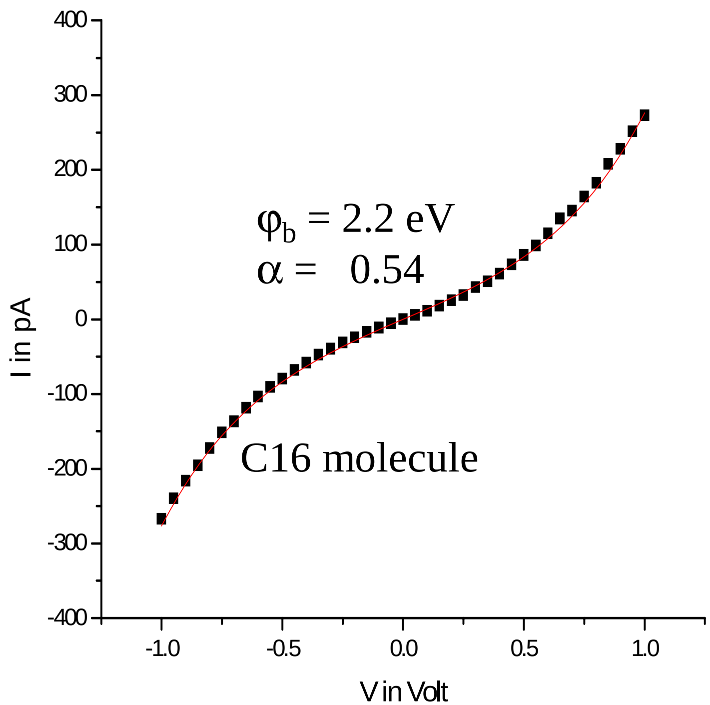
I-V Characteristics of Alkanethiol Molecules in Nanowell Device



Tunneling through SiO_2/Air

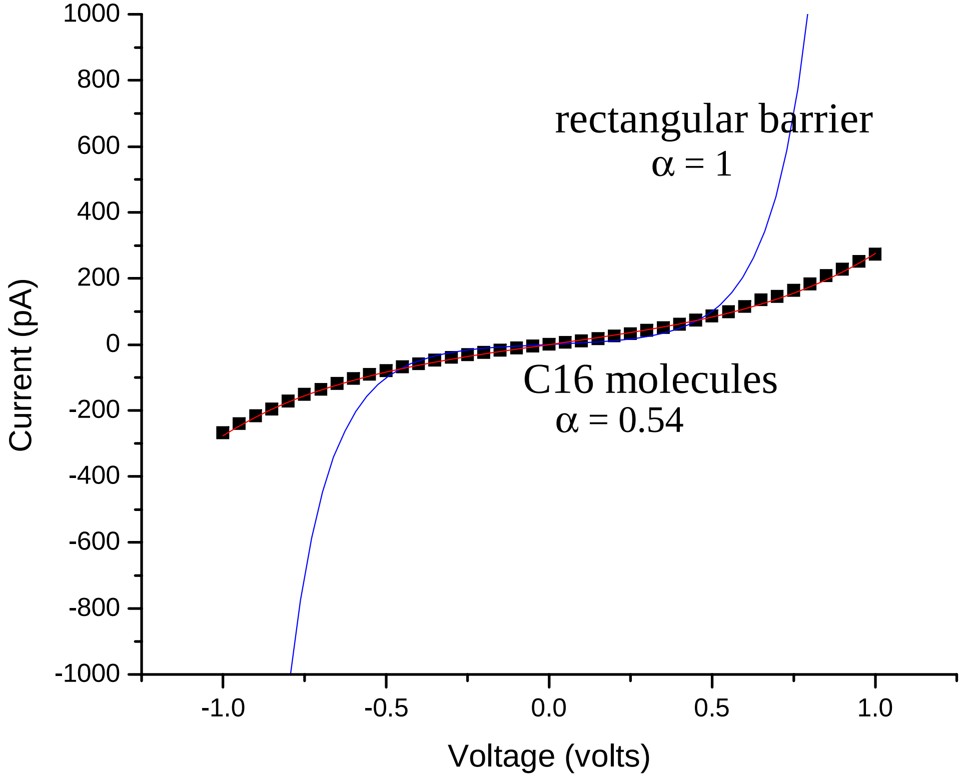
Tunneling through molecules





IV characteristics for C16 molecule

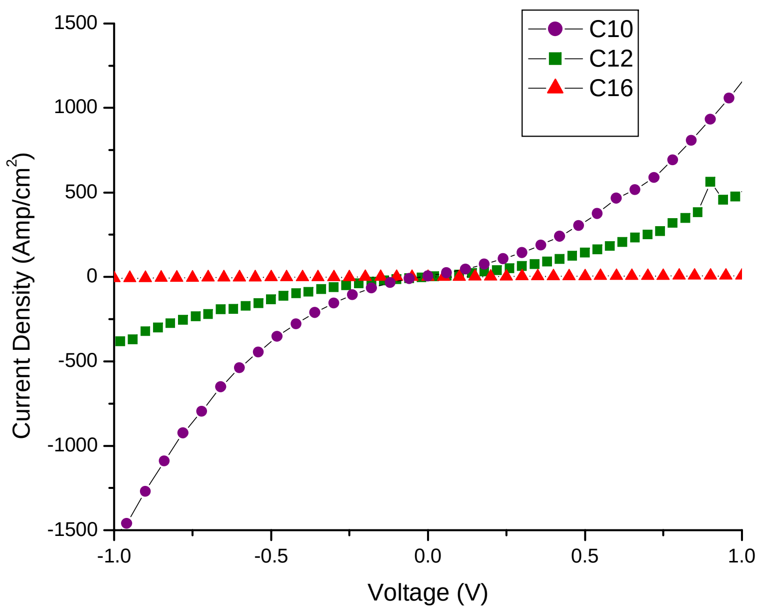
Literature value for α is .65-.68
Ref. Wang et al.



IV characteristics for C16 molecule
And a simulated curve for tunneling through
Rectangular barrier

Current Density Vs. Chain-length

Molecule	Average Φ (eV)	Average α
C16	**2.1 +/-0.1**	**0.56 +/- 0.02**
C12	**2.1+/- 0.1**	**0.55+/- 0.05**
C8 (monothiol)	**2.1+/- 0.1**	**0.77+/- 0.05**
C8 (dithiol)	**2.05+/- 0.15**	**0.72+/- 0.04**
Literature Values	**1.42 eV*** **2.2 eV+**	**0.66 for C12*** **0.68 for C16***



• W. Wang, T. Lee, and M. A. Reed, *Phys. Rev. B* **68**, 035416 (2003)

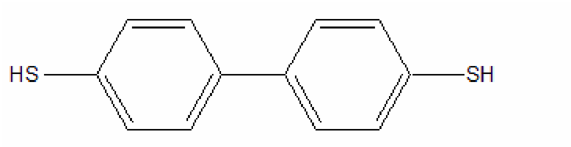
+ D. J. Wold and C. D. Frisbie, *J. Am. Chem. Soc.* **123**, 5549 (2001)

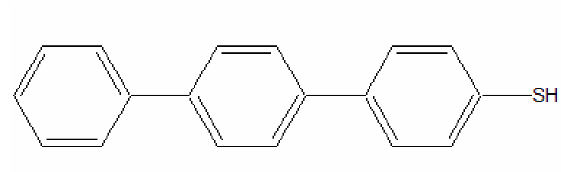
σ X. D. Cui, et al., *Nanotechnology* **13**, 5 (2002)

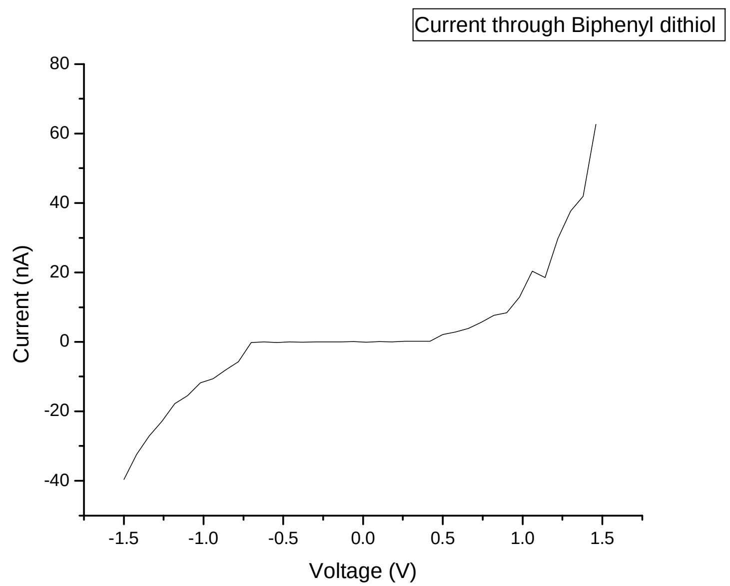
- Current density has an exponential dependence on chain length
- Our exponential decay factor β = 0.7 to 0.75 / Å

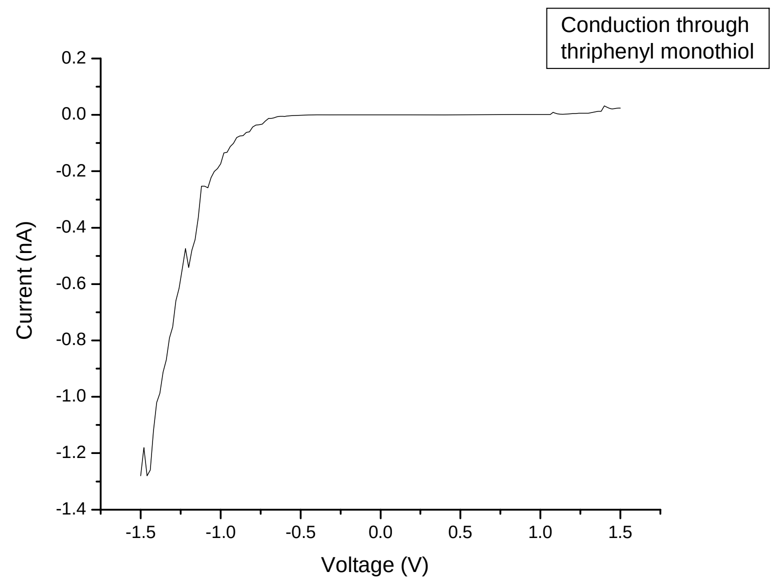
literature values : 0.72/Å to 0.83 / Å *, 0.8±.2/ Åσ

Electrical characteristics of conjugated molecules

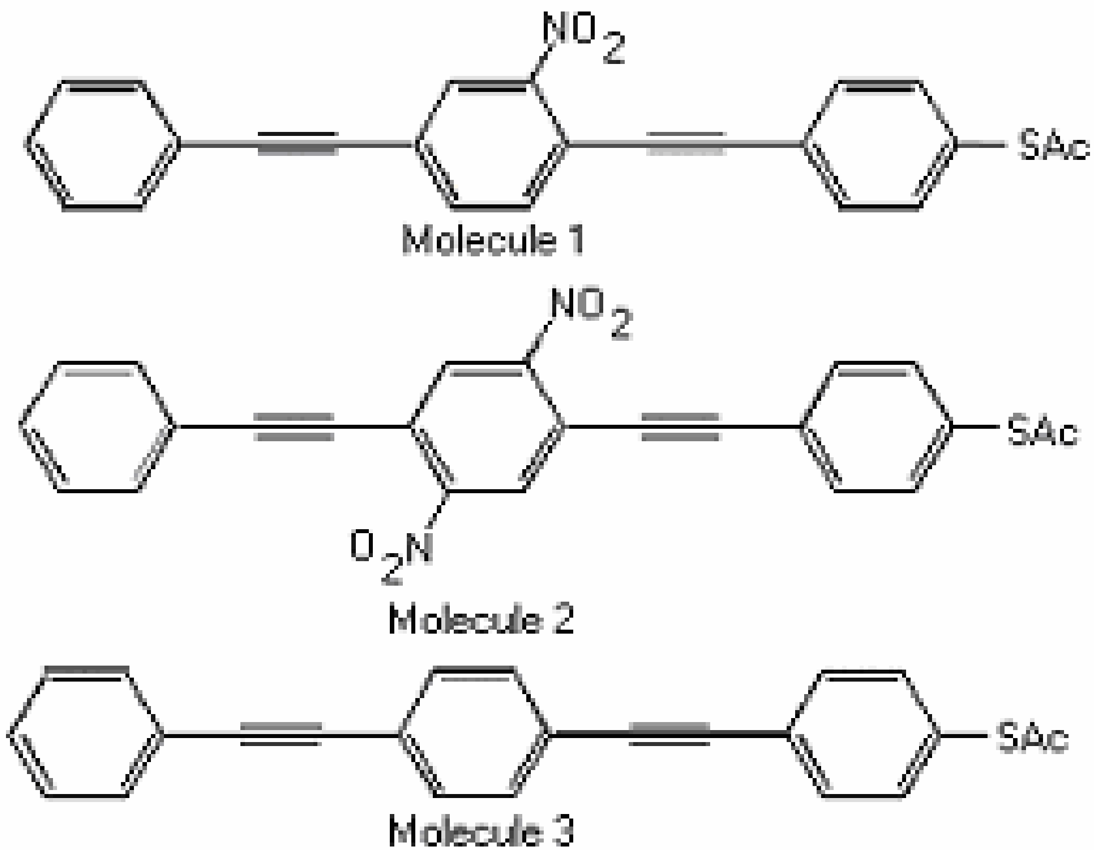






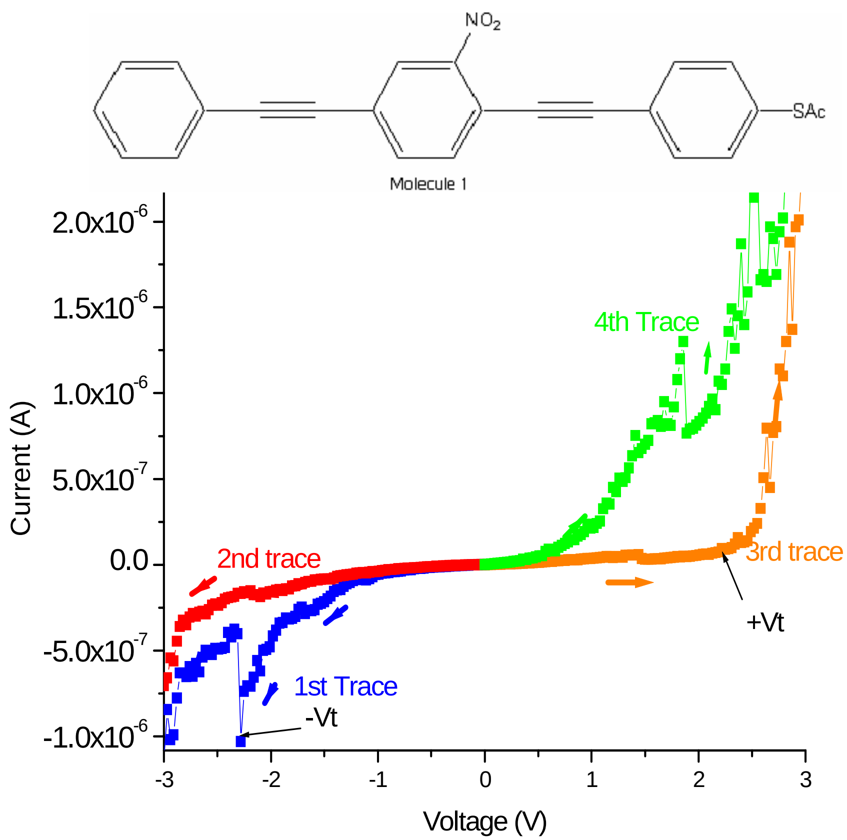


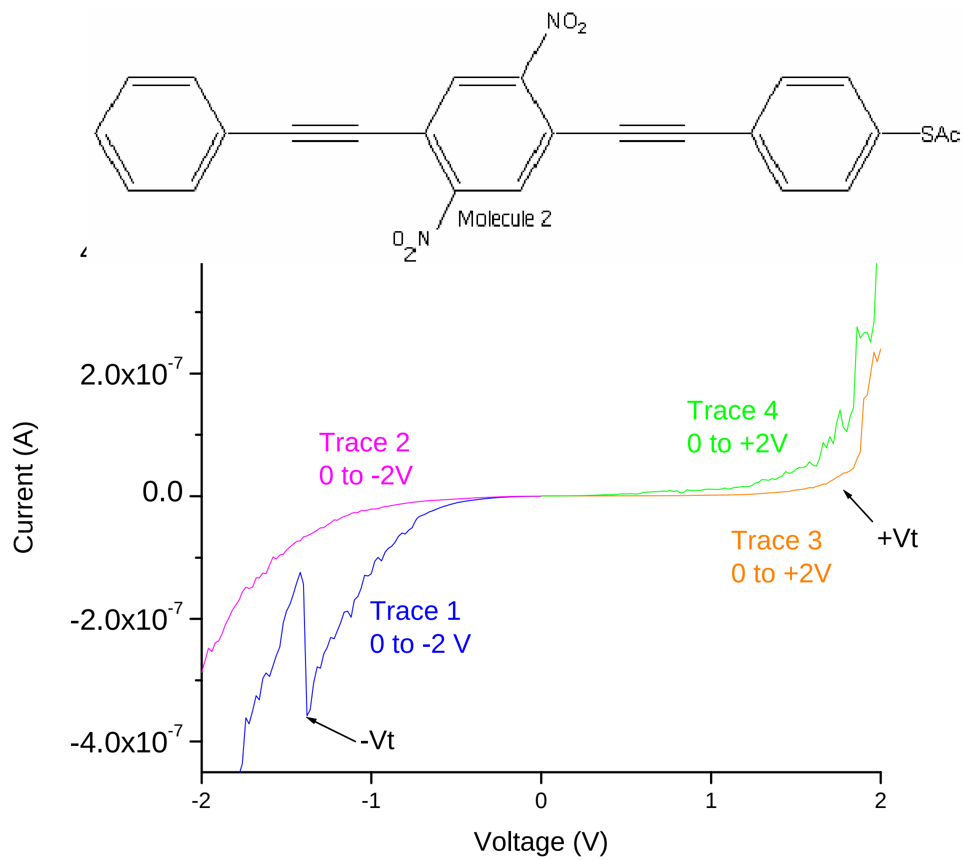
Ref. N. Majumdar et al., J. Vac. Sci. and Technol. B, July-August (2005).



Three different molecules tested in the nanowell test device. Molecule 1 is an OPE molecule with one nitro side group. Molecule 2 is an OPE molecule with two nitro side groups. Molecule 3 is an OPE molecule with no nitro side groups. The acetate moieties were removed by acid treatment to produce the free thiols for assembly.

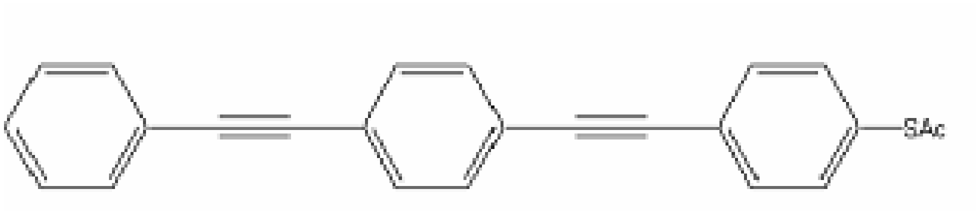
I-V Characteristics from the Nitro Molecule

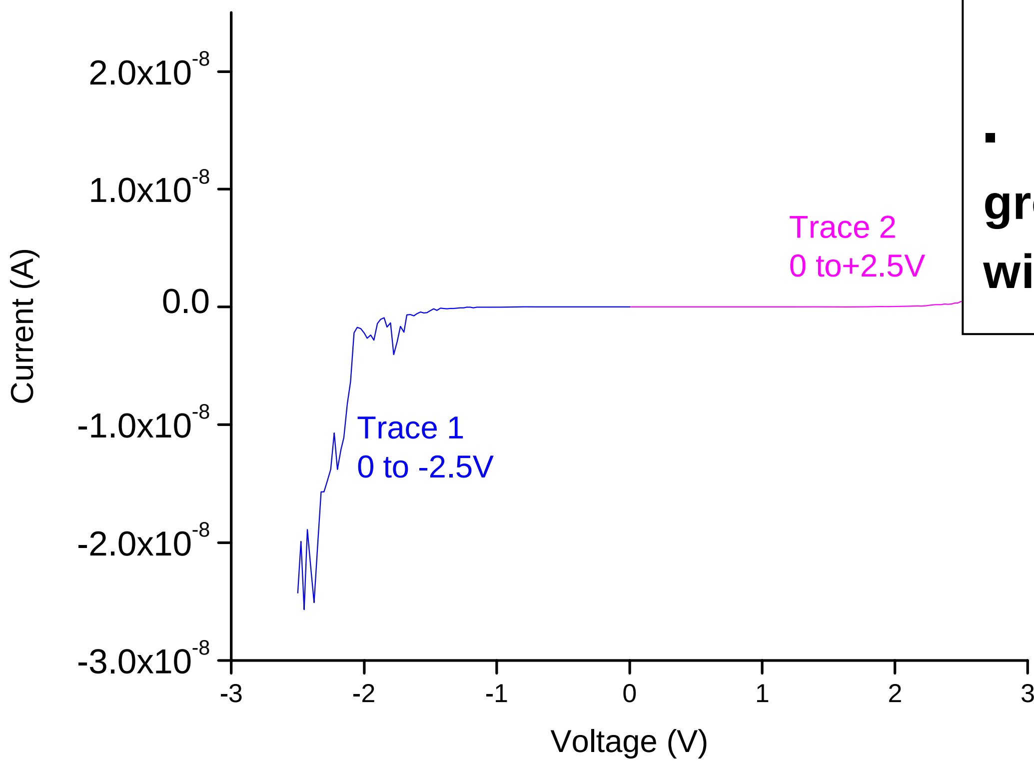




Ref. N. Gergel et al, J.Vac. Sci. and Technol A, July-August, 2005.

Results from an OPE without the Nitro Group

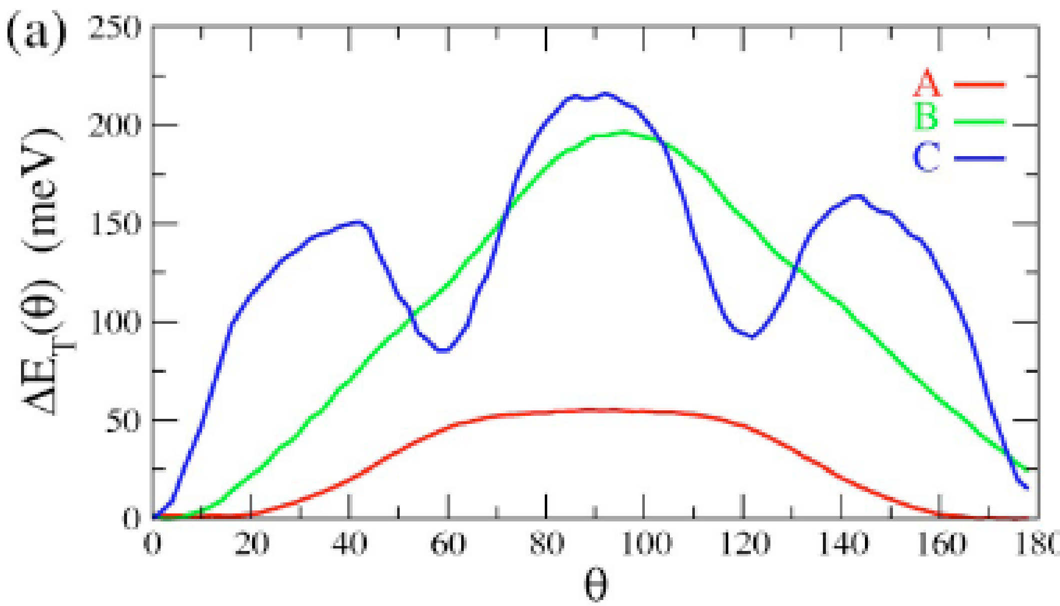




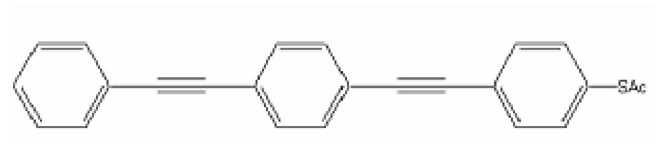
- **No switching with memory observed**
- **Expected rectification behavior observed**
- **Irreversible break down was seen beyond this voltage range**

- ***Conclusion:* Presence of nitro group is necessary for switching with memory**

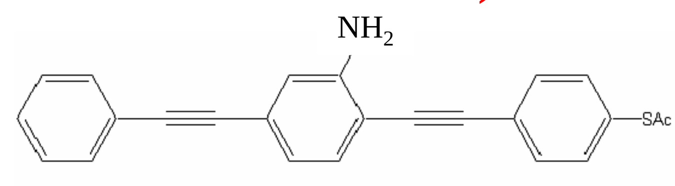
Energy vs. rotation angle



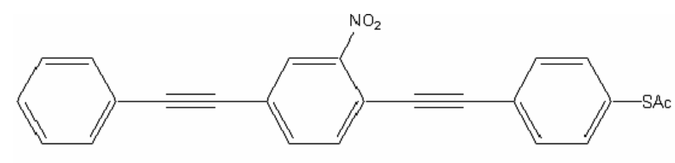
Ref. Stokbro et al.,
Phys. Rev. B 68, 121101 (2003).



A (OPE)



B (Amine)



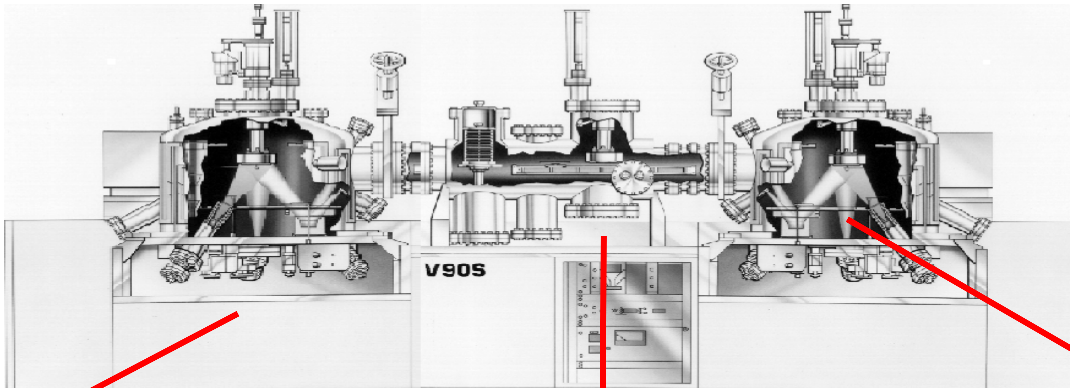
C (Nitro)

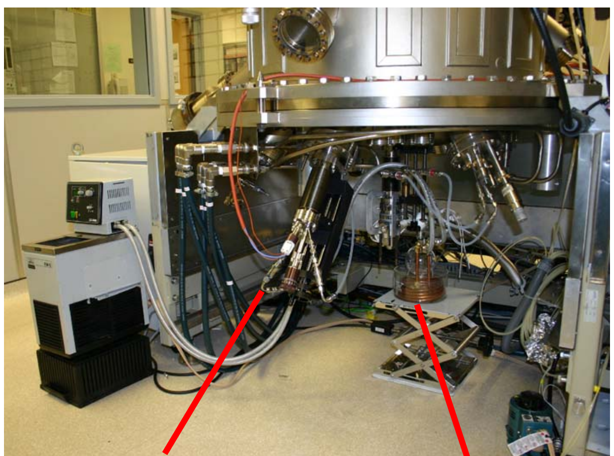
- Twisted configuration at 60º may be stable for only nitro molecules
- This configuration not stable when intermolecular distance increases
- Possible hydrogen bonding stabilizes the twisted conformation

Integration Challenges

- **Temperature <100^{o}C**
- **No external force**
- **No ultrasonic wave application**
- **Phtolithography performed before growing molecules**
- **Minimum exposure to air**

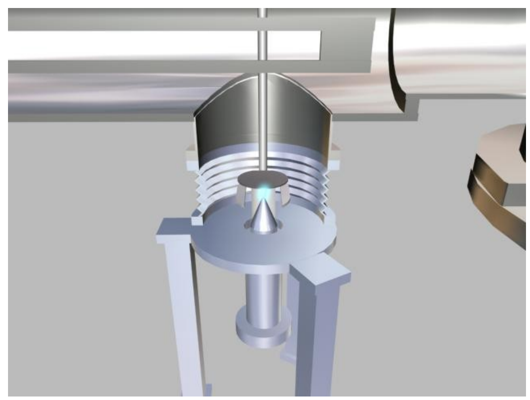
UVA Dual Growth Chamber VPD / MBE System



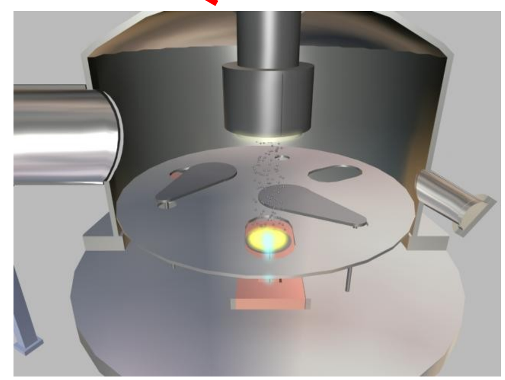


Low T molecular evaporation cell

Liquid molecular leak source & temperature bath

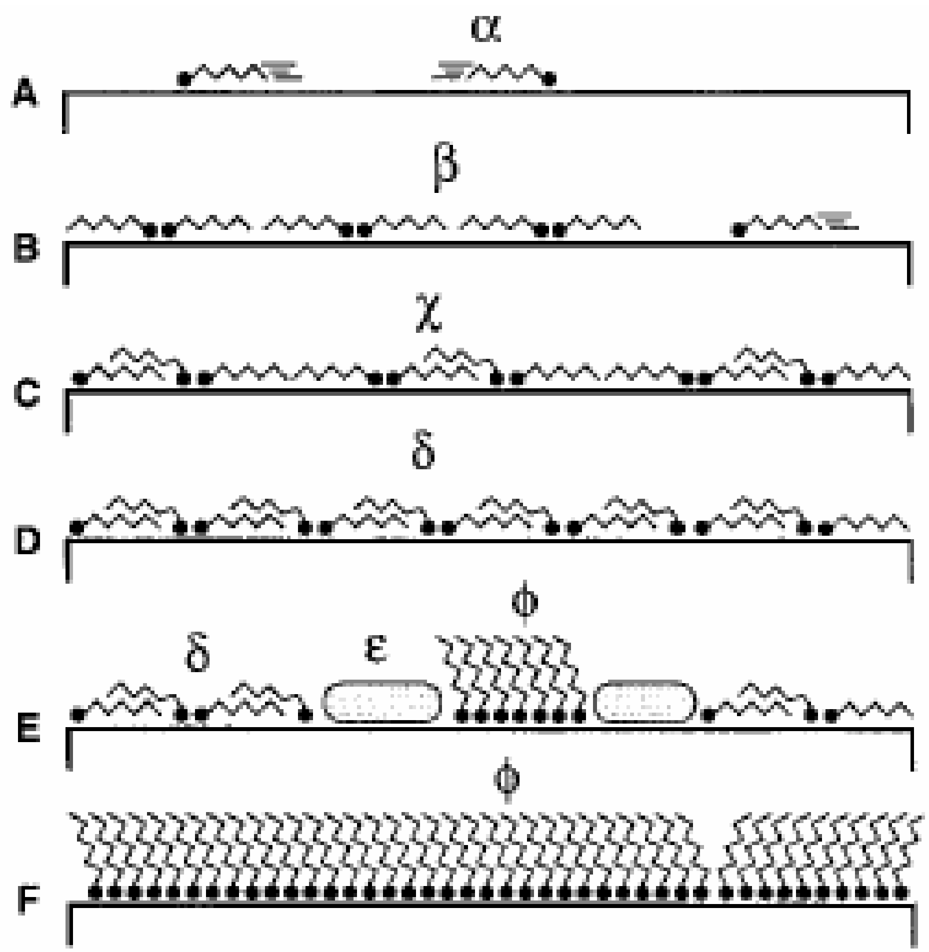


In-situ Ga^{+} focused ion beam patterning system (30-50 nm resolution)



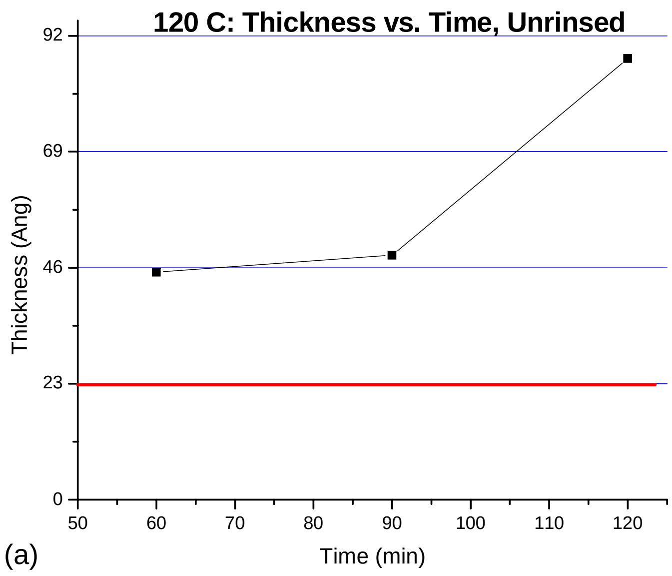
Si / SiGe MBE system w/ dual low-E ion implanter

Self-Assembled Monolayers from Vapor Phase

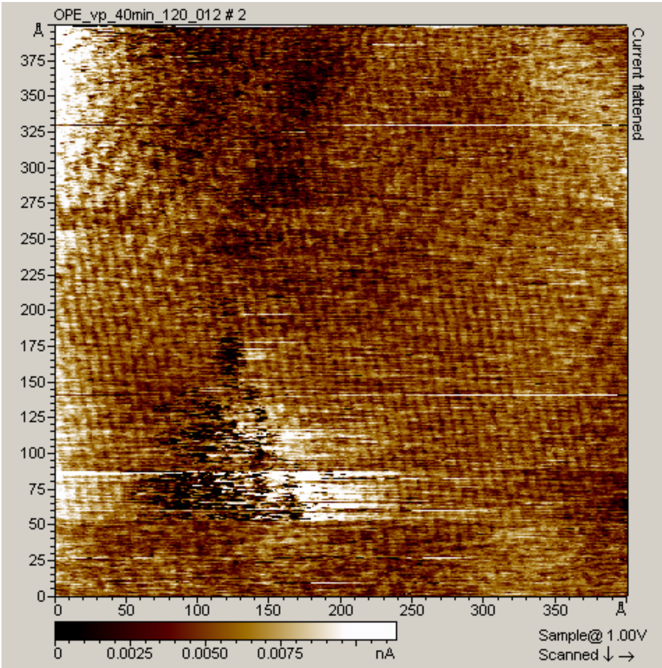


Shreiber, *Progress in Surface Science* **65**, 151(2000).

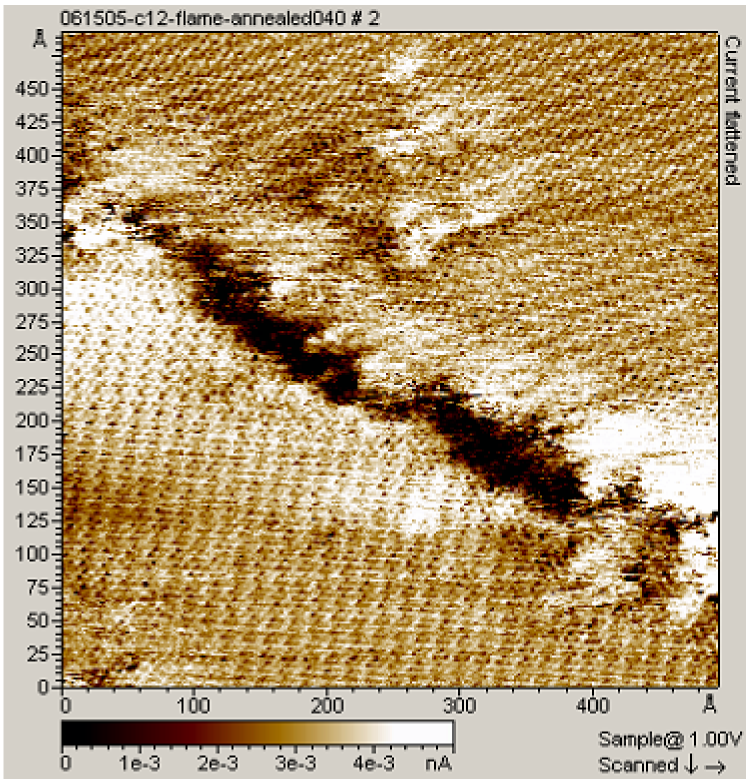
Vapor Phase OPE Molecule Deposition

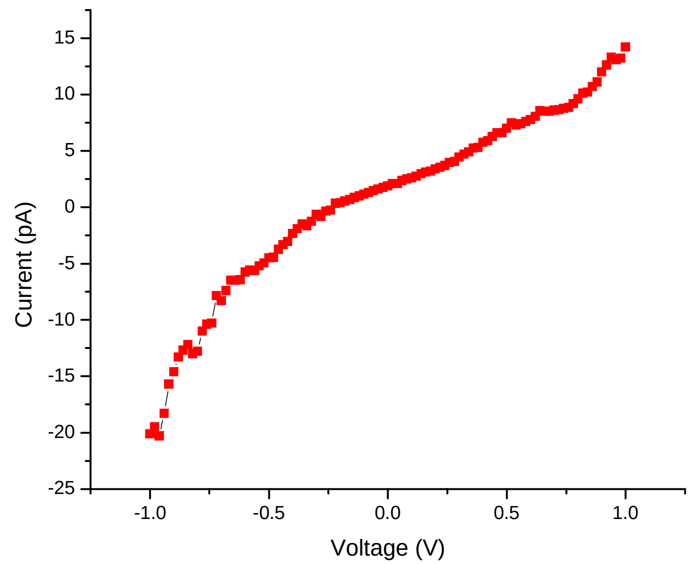


(a)



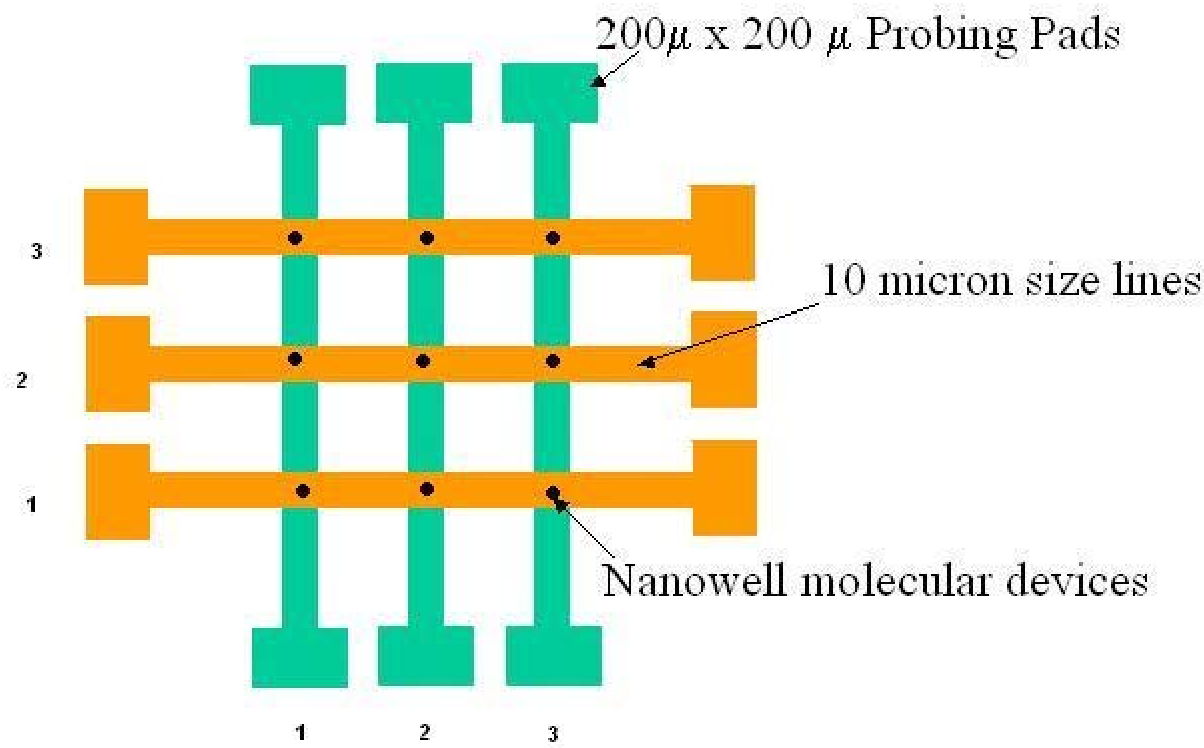
Vapor Phase C12 Alkanethiol Deposition



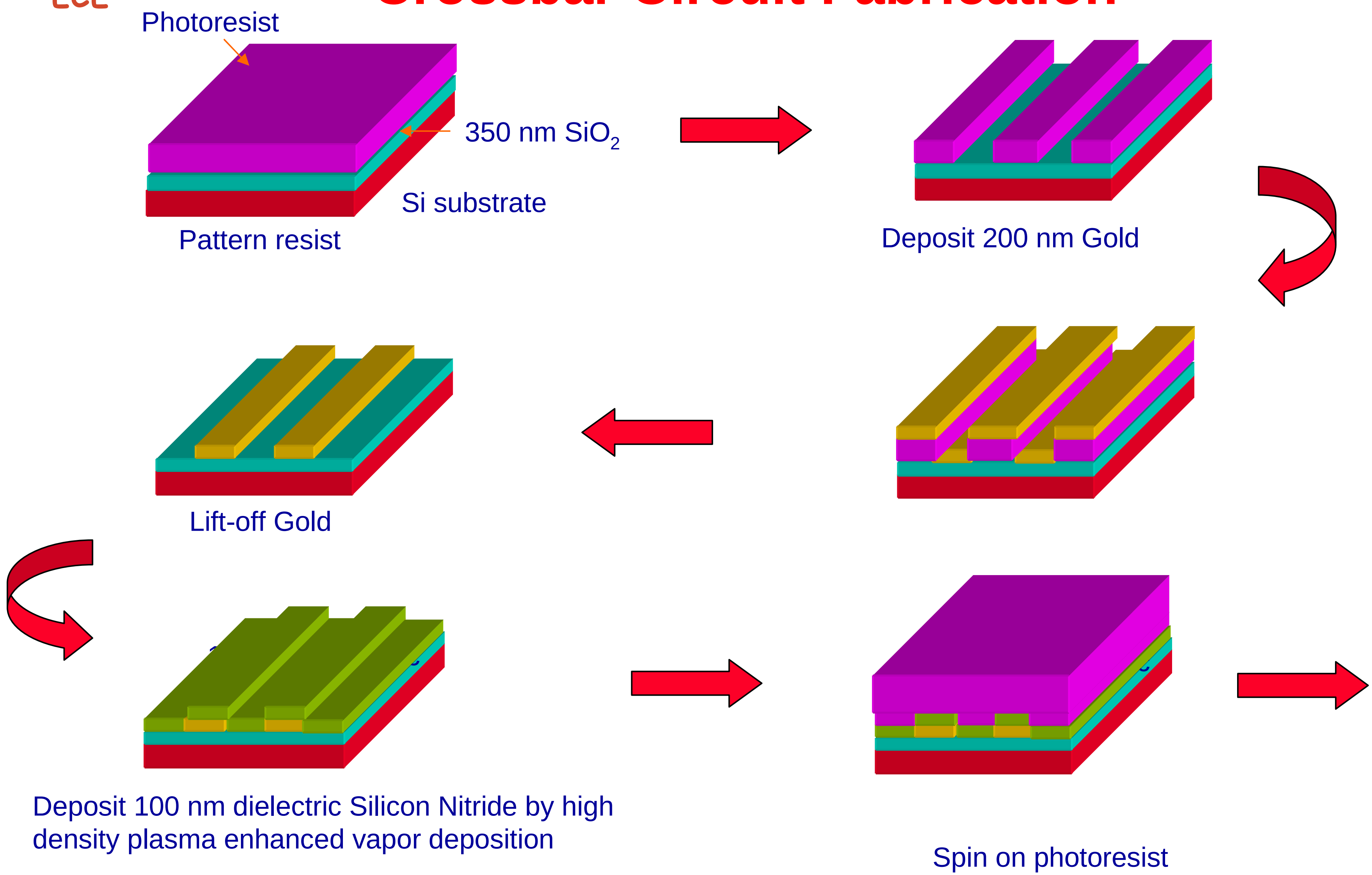


STM image of C12 on flame-annealed Au assembled via vapor phase deposition. I-V characteristic of Nanopore made with vapor deposited C12.

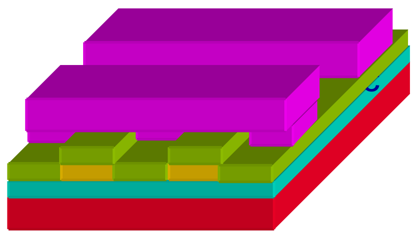
Layout of a 3x3 crossbar circuit



Crossbar Circuit Fabrication

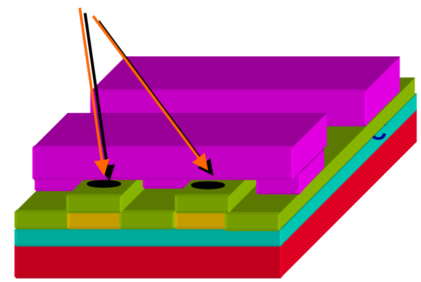


Crossbar Fabrication (cont'd)



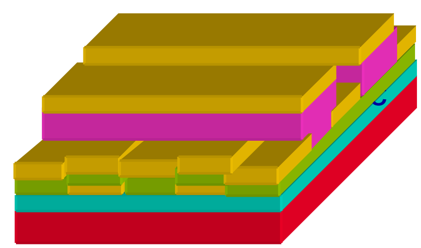
Pattern photoresist

Nanowells



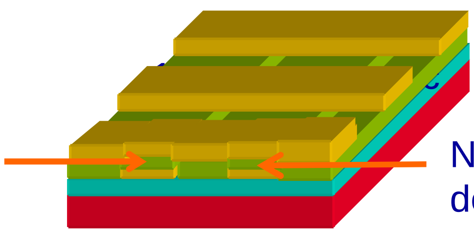
Ion mill 100 nm x 100 nm nanowells through nitride

Deposit molecules from vapor phase



Deposit 200 nm thick Gold layer

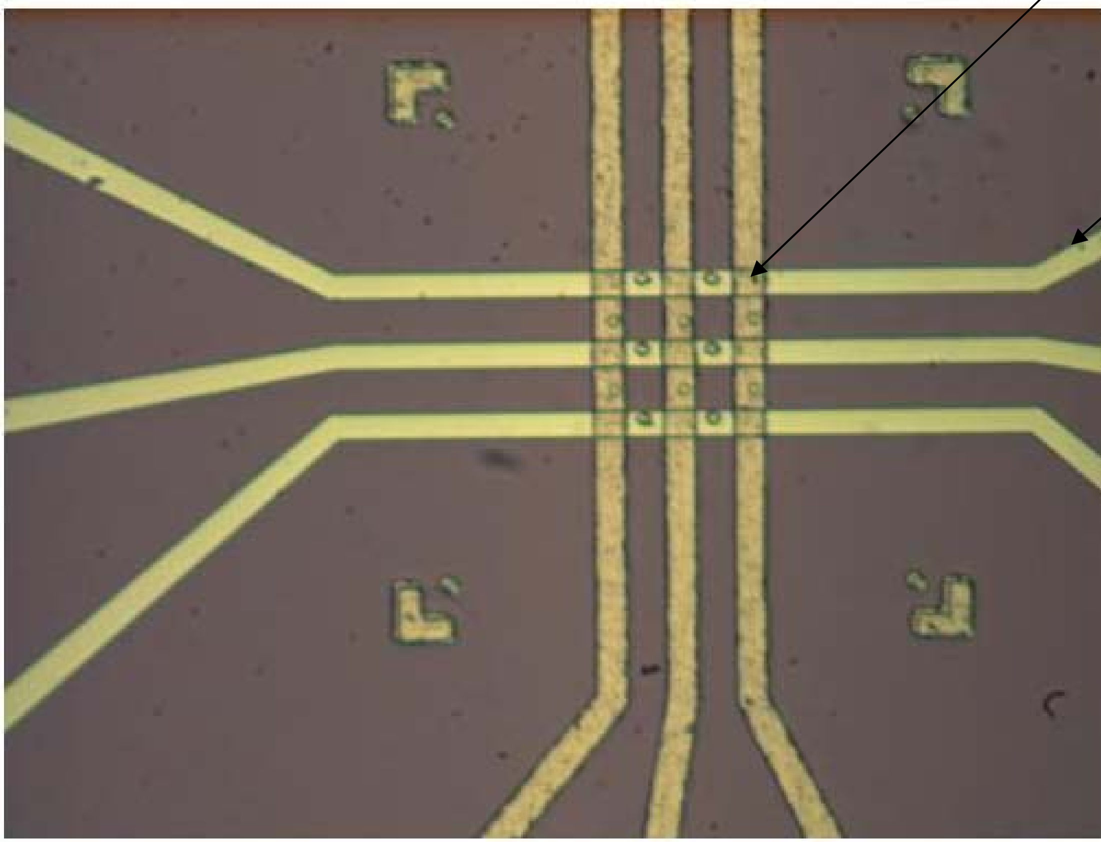
Nanowell device



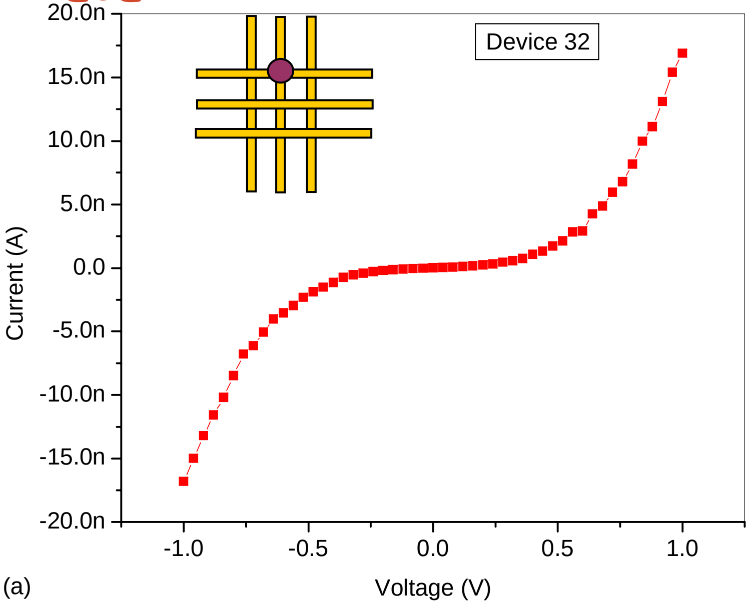
Nanowell device

Lift-off at room temperature

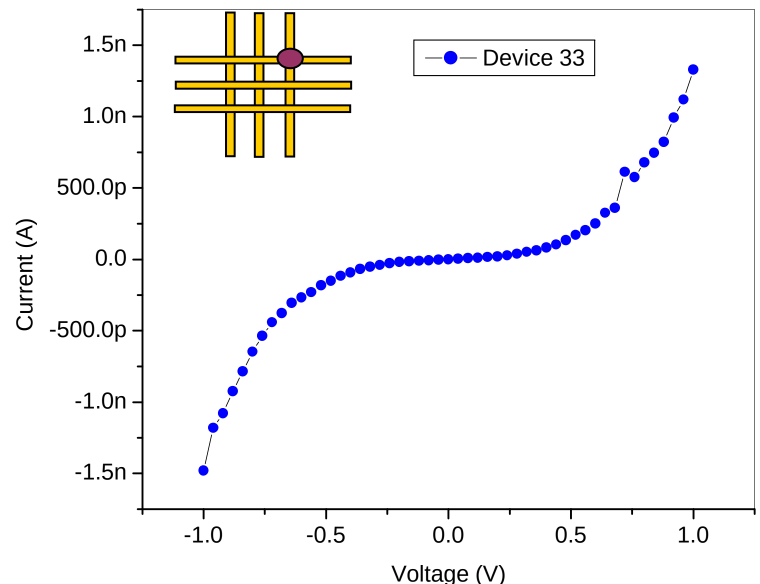
Optical Micrograph of Crossbar



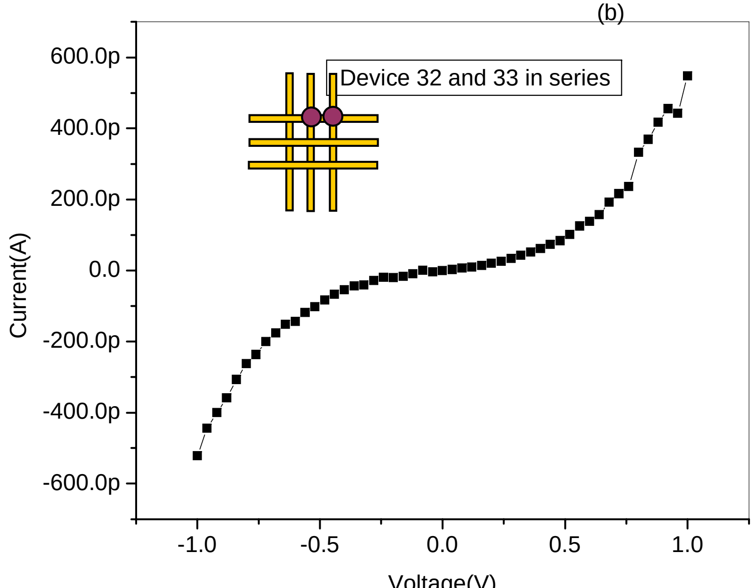
Tesing devices connected in series



(a)



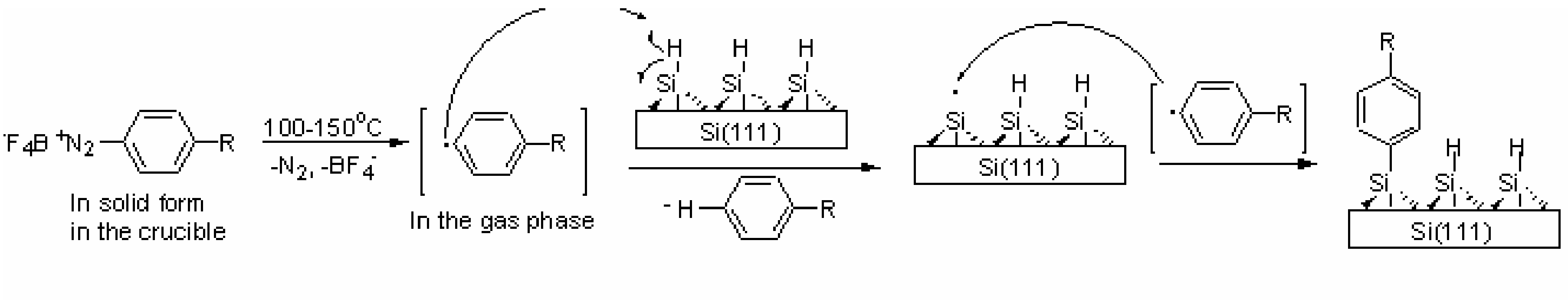
(b)



(c)

Polycrystalline Au Limits Yield…..

Vapor Phase Molecular Deposition on Silicon Using Diazonium Chemistry



Si Nanopore

SOI Wafer

Molecular Electronics Summary

- Planar device structure enables many molecules to be evaluated
- Metal-molecule interface is critical
- Switching mechanism experiments consistent with H-bonding model
- Yield limited by polycrystalline metal films - *conductive polymer top contact interlayer*
- Vapor Phase Assembly and planar device enables circuit fabrication
- Vapor Phase Molecular assembly on single-crystal Si, GaAs is very promising

<u>Early Days – Lots of room for improvement</u>